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# Scaling theory and enthalpy of mixing for binary fluids

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Binary liquids often show phase separation upon heating and cooling (Fig. 1). The critical point associated with the first behavior is called LCST (lower critical solution temperature), whereas the one associated with the latter behavior is called UCST (upper critical solution temperature). Polymer solutions in particular exhibit almost universally this type of phase behavior. In compatible polymer blends on the other hand, only LCST can be found in general, although in many cases thermal degradation of one of the components intervenes before the phase separation can be observed. However, for mixtures of polymers which are very much alike, a UCST is possible,<sup>1,2</sup> but direct observation is very difficult because of the relatively high glass transition temperature of polymers. Criteria which discriminate between UCST and LCST and which can be tested below the glass transition temperature are therefore of considerable importance. One such criterium is associated with the sign of the enthalpy of mixing. The direct determination of the latter for polymer-polymer mixtures is very awkward and obviously impossible below the glass transition temperature of the blend. The required parameters can, however, be obtained from differential heat of solution measurements.<sup>3</sup>

From a classical thermodynamic analysis it follows that apart from exceptional cases, mixing is exothermic near an LCST and endothermic near an UCST. A

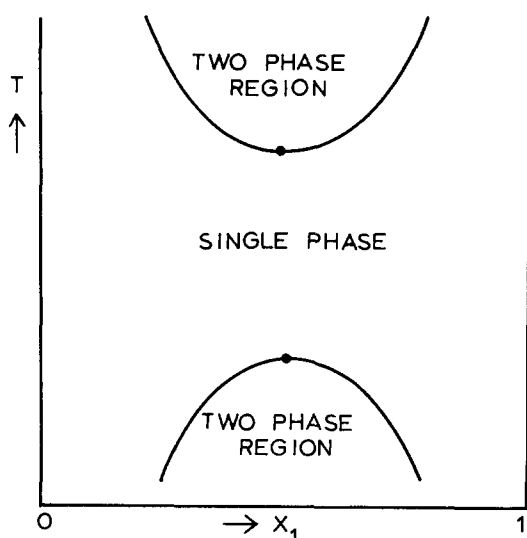


FIG. 1. Coexistence curves for a binary mixture showing phase separation at high and at low temperatures; critical points are indicated by dots,  $T$  is the temperature and  $x_1$  the mole fraction of component 1.

crucial assumption in all the derivations of this result is that the free energy can be expanded in a Taylor series at the critical point.<sup>4-6</sup> It is, however, generally recognized that the thermodynamic quantities depend nonanalytically on their variables at the critical point. It is the purpose of this note to give an alternative derivation of the aforementioned result based on the well-known scaling laws.<sup>7,8</sup>

For a binary fluid let  $\mu_1$  and  $\mu_2$  be the chemical potentials of the two components. Following Griffiths and Wheeler<sup>9</sup> we write

$$\Delta = \mu_1 - \mu_2 = (\partial G / \partial x_1)_{T,p}, \quad (1)$$

where  $G$  is the Gibbs free energy and  $x_1$  is the mole fraction of component 1. The scaling hypothesis leads to the following equation of state<sup>7,8</sup>:

$$\Delta(T, x_1) - \Delta(T, x_{1c}) = \Delta x_1 |\Delta x_1|^{\delta-1} h(y), \quad (2)$$

where  $\Delta x_1 = x_1 - x_{1c}$ ,  $\Delta T = T - T_c$ , and  $y = \Delta T / |\Delta x_1|^{1/\beta}$ .  $\beta$  is the exponent of the coexistence curve and  $\delta$  the exponent of the critical isotherm. A necessary condition for phase stability in a binary mixture is given by  $(\partial^2 G / \partial x_1^2)_{T,p} > 0$ . Combining Eqs. (1) and (2) we find

$$(\partial^2 G / \partial x_1^2)_{T,p} = |\Delta x_1|^{\delta-1} [\delta h(y) - (y/\beta) h'(y)], \quad (3)$$

where  $h'(y)$  is the first derivative of  $h(y)$ . Phase stability therefore requires

$$\beta \delta h(y) > y h'(y). \quad (4)$$

On the coexistence curve  $y$  has a fixed value  $y_0$  corresponding to  $h(y_0) = 0$ . Together with Eq. (4) this implies  $y_0 h'(y_0) < 0$ . This results in two different situations:

$$h'(y_0) \begin{cases} > 0 \rightarrow \text{UCST}, \\ < 0 \rightarrow \text{LCST}. \end{cases} \quad (5)$$

Consider the entropy  $S$  of a binary fluid. Let the superscripts ' and '' denote the two coexisting phases near the critical point. From thermodynamics we know

$$\begin{aligned} (\partial S / \partial x_1)' - (\partial S / \partial x_1)'' &= -(\partial / \partial T) [\Delta(T, x_1') - \Delta(T, x_{1c})] \\ &\quad + (\partial / \partial T) [\Delta(T, x_1'') - \Delta(T, x_{1c})]. \end{aligned} \quad (6)$$

Together with the scaled equation of state 2 this results in

$$(\partial S / \partial x_1)' - (\partial S / \partial x_1)'' = -2 \Delta x_1' |\Delta x_1'|^{(\gamma-1)/\beta} h'(y_0), \quad (7)$$

where  $\gamma = \beta(\delta - 1)$ . According to this equation and the properties listed in expression (5), UCST and LCST behavior differ in a fundamental way. If the superscripts prime and double prime correspond to the left and right branch of the coexistence curve, we have  $\Delta x_1' < 0$  (Fig. 1)

and :

$$(\partial S / \partial x_1)' - (\partial S / \partial x_1)'' \begin{cases} > 0 \rightarrow \text{UCST} , \\ < 0 \rightarrow \text{LCST} . \end{cases} \quad (8)$$

If there is no inflection point in the entropy curve, it follows that the entropy of mixing  $\Delta S_m$  defined by  $\Delta S_m(x_1) \equiv S(x_1) - [x_1 S(1) + (1 - x_1) S(0)]$ , is positive near an UCST and negative near an LCST.<sup>2</sup>

To obtain a similar result for the enthalpy  $H$  we note that

$$\mu'_i - \mu''_i = h'_i - h''_i - T(s'_i - s''_i) = 0 , \quad (9)$$

where  $h_i$  and  $s_i$  ( $i = 1, 2$ ) denote the partial molar enthalpy and partial molar entropy, respectively. Therefore, we also have

$$(\partial H / \partial x_1)' - (\partial H / \partial x_1)'' \begin{cases} > 0 \rightarrow \text{UCST} , \\ < 0 \rightarrow \text{LCST} . \end{cases} \quad (10)$$

Again it follows that the enthalpy of mixing  $\Delta H_m$ , defined by  $\Delta H_m(x_1) \equiv H(x_1) - [x_1 H(1) + (1 - x_1) H(0)]$ , is positive near an UCST and negative near an LCST provided the enthalpy curve has no inflection points. Although this cannot be precluded, in general it is rather uncommon. The

derivation shows that these properties are a simple consequence of the stability condition and the assumption of symmetry embodied in Eq. (2) which, although less well satisfied far from the critical point than is the analogous assumption in pure fluids, will be valid extremely close to the critical point.

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## On the lowest sigma and pi anion states of Be<sub>2</sub> and Be<sub>3</sub>

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The group IIA and IIB metal atoms are known to have low-lying (i.e., slightly unbound) <sup>2</sup>P temporary anions,<sup>1,2</sup> raising the possibility that small clusters of these atoms will possess stable anions resulting from electron addition to low-lying molecular orbitals dominated by the atomic *p* orbitals. Previous calculations<sup>3,4</sup> have indicated that the ground state anions of Be<sub>2</sub> and Be<sub>3</sub> are bound and are due to the occupation of the *p<sub>σ</sub>* rather than the *p<sub>π</sub>* orbitals. However, since the basis sets utilized were restricted to *s* and *p* functions and since it has recently been found that correlation effects involving *d* functions are important in the bonding of neutral beryllium and magnesium<sup>5,7</sup> clusters, we have performed new calculations of the electron affinities (E.A.) of Be<sub>2</sub> and Be<sub>3</sub> using [10s4p/5s2p] (*sp*) and [10s4p1d/5s2p1d] (*spd*) contracted Gaussian basis sets. The *s* and *p* functions are the same as those employed in Ref. 4. The exponent of the *d* function is taken to be 0.20, the value which minimizes the energy of the 1s<sup>2</sup>2s2p(<sup>1</sup>P) state in a configuration interaction calculation.

Self-consistent field (SCF) calculations on the open and closed shell species are performed using the spin-restricted and spin-unrestricted SCF procedures,<sup>8</sup> respectively. The role of electron correlation is then investigated using second-order many-body perturbation theory (PT). We recognize from the onset that quantitative results are not expected at this level of treatment. Our objective here is to emphasize the *qualitative* changes brought about upon the inclusion of *d* functions in the atomic basis set.

In Fig. 1 we display the SCF and PT potential energy curves of <sup>1</sup>Σ<sub>g</sub><sup>+</sup>Be<sub>2</sub> and the <sup>2</sup>Σ<sub>g</sub><sup>+</sup>(1σ<sub>g</sub><sup>2</sup>1σ<sub>u</sub><sup>2</sup>2σ<sub>g</sub><sup>2</sup>2σ<sub>u</sub><sup>2</sup>3σ<sub>g</sub>) and <sup>2</sup>Π<sub>u</sub>(1σ<sub>g</sub><sup>2</sup>1σ<sub>u</sub><sup>2</sup>2σ<sub>g</sub><sup>2</sup>2σ<sub>u</sub><sup>2</sup>1π<sub>u</sub>) states of Be<sub>2</sub><sup>-</sup>. We first consider the SCF results. With the *sp* basis the minimum in the <sup>2</sup>Σ<sub>g</sub><sup>+</sup>Be<sub>2</sub><sup>-</sup> curve lies energetically below the Be<sub>2</sub> potential curve, while that in the <sup>2</sup>Π<sub>u</sub> curve lies above the Be<sub>2</sub> curve. The addition of *d* functions stabilizes both anion curves relative to that of the neutral molecule (with a slightly greater effect for the <sup>2</sup>Π<sub>u</sub> curve) giving rise to small (~0.05 eV) increases in the E.A.'s.